HOT-FILAMENT ASSISTED DEPOSITION OF DIAMOND IN THE VAPOR OF METHANOL-BASED LIQUID SOLUTIONS

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ABSTRACT

A method for depositing diamond crystals and diamond films in the vapor of methanol-based solutions is reported. The methanol-based solution contains a few percent by weight of one or more carbon containing compounds that have the ratio of carbon to oxygen being greater than one. A hot filament is applied to dissociate the vapor of the premixed solution and generate oxidizing and etching radicals such as OH, O, H as well as carbon depositing radicals such as CH_3. Graphitic and amorphous carbon deposition is suppressed or preferentially etched resulting in the net deposition of good quality diamond crystals and diamond films.

1. INTRODUCTION

Chemically vapor deposited diamond has many unique and outstanding properties that make it an ideal material for a broad range of scientific and technological applications [1]. A number of methods for chemical vapor deposition of diamond based on varied gas mixtures and energy sources for dissociating the gas mixtures have been reported [2]. These techniques include the use of high-temperature electrons in various kinds of plasmas, high-temperature surfaces of hot filaments, and high-temperature gases in combustion flames to dissociate molecular hydrogen, oxygen, halogen, hydrocarbon, and many other carbon containing gases. The substrate is usually maintained at a temperature much lower than that of electrons in a plasma, the hot filaments, or the combustion flame, resulting in a super equilibrium of atomic hydrogen near the diamond growing surface.

Most diamond chemical vapor deposition processes involve the use of hydrogen gas or some kind of hydrogen containing molecules. The most typical diamond CVD process uses methane gas diluted by 94-99.9% hydrogen. The super equilibrium of atomic hydrogen can be achieved in a gas mixture with varied percentage of molecular hydrogen depending on the balance between the effectiveness of the dissociation process in generating atomic hydrogen and the loss processes for atomic hydrogen to recombine or react with other radicals. By the use of a high-power-density microwave plasma, atomic hydrogen is very effectively generated from molecular hydrogen and diamond can be deposited in a mixture of methane diluted by less than 50% hydrogen [3] Growth of diamond from oxy-acetylene flames uses acetylene and oxygen with the ratio of acetylene to oxygen slightly greater than 1 without needing molecular hydrogen. Diamond is deposited in the reducing "inner flame" where atomic hydrogen is produced by the high temperature flame as one of the burn products. In addition to atomic hydrogen, there are plenty of OH radicals present near the diamond-growing surface inside the flame.

Oxidizing radicals such as OH and O can play some roles of atomic hydrogen in the diamond growth process, i.e., preferential etching of non-diamond carbon resulting in a net deposition of high purity diamond. Small quantity of oxygen (0.5-2%) or water vapor (<6%) added to the methane and hydrogen mixture has been reported to improve diamond crystallinity and to lower the diamond deposition temperature [4,5] The quantity of oxygen and water in a feedstock is a relative term depending on other process parameters. Diamond has been grown in a microwave plasma of acetone/oxygen mixture with molecular ratio near 1:1 [6].

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Hot filaments were applied to convert the vapor of methanol-based liquid solutions into favorable mixtures of species for diamond nucleation and growth without any addition of compressed gases. Diamond of excellent quality has been deposited on silicon substrates at a substrate temperature near 700-900C. This liquid only process is economic, safe but the processing parameter space is narrow due to the oxidizing environment for hot filaments.

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Most of diamond CVD processes use one or more compressed gases. These gases usually must be precisely controlled using electronic mass flow controllers to ensure an accurate composition in the gas feed. Rudder et al. reported the success in the growth of diamond using a RF plasma in a mixture of water (more than 40%) and alcohol [7]. No compressed gases were needed for this diamond deposition process.

Rudder et al [7] conducted an experiment and concluded that the hot-filament assisted CVD process using 18 sccm water and 40 sccm ethanol at 80 Torr with filament temperature at 2100°C located about 2 mm from the silicon substrate at 650°C deposited only fine grain graphite in contrary to the deposition of diamond as claimed by Komaki et al. [8]. A fine-tuning of the deposition process is necessary for the use of hot filaments for growing diamond in a gas or vapor mixture with a high oxygen or water content. In this paper, successful deposition of diamond by means of hot-filament assisted CVD technique in an environment that is rich in oxidizing radicals is reported.

2. EXPERIMENTAL

High quality diamond crystals and diamond films are deposited using a liquid solution as the feedstock and using a hot filament as the means of dissociating and reacting the vapor of the solution. A solution consisting of 90-99% of methanol and 1-10% of selected carbon containing compounds such as ethanol, isopropanol, and acetone are premixed and fed into a deposition chamber through a liquid flow controller such as a needle valve. The solution vaporizes as it enters the low pressure deposition chamber. The vapor consists of the same composition as the solution. When the vapor passes near a hot filament heated to above 2000° C, it is dissociated to generate OH, H, O, CH_3 and other carbon containing radicals.

The substrate is a sheet or wafer of silicon, typically having been polished using 1um diamond paste prior to the deposition process. Typically, the substrate is mounted at a distance from the hot filament to insure that a desired substrate temperature and composition of radicals transported from the hot filament are achieved. In the following experiments a distance of approximately 2 cm between the substrate and the tungsten filament was used. A spiral tungsten wire of 1.5mm diameter was passed with 110A 60Hz electrical current. The reactor chamber pressure was maintained at 40 Torr. The silicon substrate of about 2.5cm by 2.5cm was heated by the hot filament to about 800-1000°C as measured by a dual color optical pyrometer. Diamond was grown at a rate of about 1 um per hour when 4 grams ethanol, 2.5 grams isopropanol, or 2.5 grams acetone was mixed with 100 grams methanol and used as the feedstock.

Figure 1 illustrates the hot-filament assisted chemical vapor deposition system. As illustrated in Fig. 1, a premixed solution **6** is fed from the solution container **5** by a Teflon or metal tubing **7** through a liquid flow controller (for example, a needle valve **8**) to the inlet **3** of a stainless steel reactor chamber **1** that is typically of 6" in diameter. When the liquid solution enters the low-pressure side of the needle valve, it vaporizes to form a vapor mixture with the same molar composition as the pre-mixed solution. In addition to the inlet **3**, the reactor chamber has an outlet **4** connected to a mechanical vacuum pump (not shown) through an automatically controlled throttle valve (not shown) to maintain constant pressure throughout the deposition process, for circulating the vapor of the methanol-based solution through the reactor chamber. The vapor is maintained at a pressure within the vacuum chamber of between 1 and 760 torr, with the pressure being monitored by a pressure gauge (not shown). The range of vapor pressure may be raised above 760 torr when a liquid pump is used to pump the methanol-based solution through a flow rate controller into a reactor chamber that is heated to a temperature higher than the ambient temperature in order to allow a higher vapor pressure of the compounds contained in the solution. The range of vapor pressure may also be lowered below 1 torr when a vacuum pump of higher throughput or higher vacuum capacity such as a turbomolecular pump is used in addition to the mechanical vacuum pump used for the performance of the present experiments.

A filament made of tungsten, tantalum, graphite or other materials of high melting points is heated to a sufficiently high temperature so that the vapor of methanol-based solution is dissociated to produce etchant radicals and carbon containing radicals for diamond deposition. A tungsten filament **9** of 1.5mm in diameter was made into a spiral shape of about 2.5 cm diameter. A variable alternate current (AC) power

supply **10** feeds 110 Amperes of current at 60Hz through the filament to heat it well above 2000°C. The methanol-based solution was fed into the reactor chamber to reach a desired deposition vapor pressure before the filament was heated to its maximum operating temperature. The condition was optimized so that there is a small net deposition of carbon on the filament in order to prevent the filament from being oxidized and eroded by the etching radicals produced from the methanol-based vapor.

A substrate **2** was placed at a distance of 2 cm from the hot filament at a reactor pressure of 40 torr. The hot filament heated the substrate to a temperature between 800 and 1000°C according to a dual color optical pyrometer(not shown). A 2.5cm by 2.5cm silicon wafer of (100) orientation was polished by 1um sized diamond paste and placed on the substrate holder with three stainless steel spacer between the silicon wafer and the substrate holder. The spacer is used to increase the temperature of the silicon wafer that is 2cm away from the hot tungsten filament. The optimal distance between the substrate and the filament and the proper thermal management of the substrate vary with the reactor vapor pressure, the filament temperature, and the composition of the vapor.

2.1 Substrate pre-treatment and cleaning

4" single-side polished silicon (100) wafer was first cut into 1"x1" dies. The dies were scratched by rubbing it with diamond paste containing 1um diamond particles. The scratched silicon dies were cleaned by acetone and methanol before being loaded onto the substrate holder. No further substrate treatment and cleaning were performed.

2.2 Deposition parameters

Tungsten filament was 1.5 mm in diameter. Alternate current (AC) of 110 A at 60Hz was passed through the filament. The vapor pressure was maintained at 40 Torr. The premixed methanol-based solution was fed into the reactor chamber through a needle valve at a rate approximately equal to 10 cubic centimeter per hour. The substrate was placed at a distance of 2 cm from the hot filament. The substrate temperature was measured to be between 800 and 1000°C by means of a dual color optical pyrometer. The reflection of light from the hot filament by the silicon surface may have interference with the temperature measurement to some extent causing the temperature measurement to be nonuniform when viewing the substrate from different directions using the pyrometer. The measured substrate temperature is believed to be an overestimation of the actual bulk temperature of the silicon substrate. The deposition period is about 10 hours resulting in diamond films of about 10 um in thickness.

2.3 Diamond film characterization methods

A Normaski phase contrast optical microscope was used to examine the crystal shapes and surface morphology of the deposited films. Diamond grains with (100) or (111) facets can clearly be seen using this optical microscope. The film thickness can also be measured by examining the cross-sectional view of the films using the same optical microscope. A micro Raman spectrometer powered by an Argon ion laser was used to examine the phase purity of the deposited films. Diamond peak around 1332 cm^{-1} provided a convincing evidence that the deposited carbon films were diamond.

3. RESULTS AND DISCUSSION

When methanol alone was used as the feedstock, too much oxidation of the hot filament resulted in the gradually reduction of the filament diameter. No diamond was deposited on the substrate. When too much of ethanol, isopropanol, or acetone was added to methanol, graphite tends to coat the hot filament leading to the swelling of the hot filament. When the substrate is placed too close to the hot filament, the etchant radical concentration at the substrate surface was too high and no deposition was observed. By properly optimizing the composition of the solution, the filament temperature, the distance between the filament and the substrate, the vapor pressure, and the substrate temperature, good quality

diamond films as indicated by a sharp Raman peak near 1332 cm^{-1} and nicely faceted diamond grains seen by an optical microscope have been achieved using liquid feedstock without any compressed gas.

The hot tungsten filament dissociates methanol-based vapor and releases OH, H, O, CH_3, CH_2, ...etc. radicals for a net deposition of diamond on the silicon surface. Methanol vapor, of which the chemical symbol is CH_3OH, has the carbon to oxygen ratio being equal to one. When it is dissociated, it forms so much oxidizing radicals that there is not a net deposition of diamond on the substrate. Instead, the tungsten filament is oxidized and eroded causing the coating of some non-diamond materials on the substrate. When a proper quantity of a carbon containing compound, such as ethanol, isopropanol, and acetone, with carbon to oxygen ratio higher than that of methanol is added to the solution, a net deposition of diamond on the substrate and the prevention of the etching of the tungsten are achieved. Ethanol, of which the chemical symbol is CH_3CH_2OH, has the carbon to oxygen ratio of 2. Isopropanol, of which chemical symbol is $(CH_3)_2CHOH$, has the carbon to oxygen ratio of 3. Acetone, of which the chemical symbol is CH_3COCH_3 ,has the carbon to oxygen ratio of 3.

In the conducted experiments, the deposition process lasted for 10-14 hours resulting in diamond films with well faceted diamond grains clearly visible using an optical microscope. The diamond grain size was around 10 um in size indicating that the diamond growth rate was in the order of 1um per hour.

As an example a methanol-based solution was prepared by mixing 4 grams of ethanol with 100 grams of methanol. Other experimental parameters were the same as that described in the Experimental Section. Figure 2 shows the optical micrograph of the deposited diamond film. A diamond film with well faceted diamond grains can be clearly seen in Figure 2. Raman spectrum shown in Figure 3 clearly indicates that a sharp diamond peak at around 1332 cm^{-1} is present and the deposited diamond film is of good quality. Similar results were obtained using other solutions such as a mixture of isopropanol alcohol and methanol and a mixture of acetone and methanol.

4. CONCLUSIONS

A hot-filament assisted chemical vapor deposition technique using methanol-based solutions as the feedstock has been reported for the deposition of diamond crystals and diamond films. The OH, H, O radicals generated by the dissociation of the methanol-based vapor were proven to be sufficient in suppressing the growth of graphitic and amorphous carbon resulting in the net deposition of diamond by the carbon containing radicals that were dissociated from the same vapor. By the addition of a few weight percentage of carbon containing compounds with carbon to oxygen ratio greater than one to the methanol, the erosion of the hot tungsten filament by the strongly oxidizing and etching radicals released from the vapor after being dissociated by the hot filament was eliminated.

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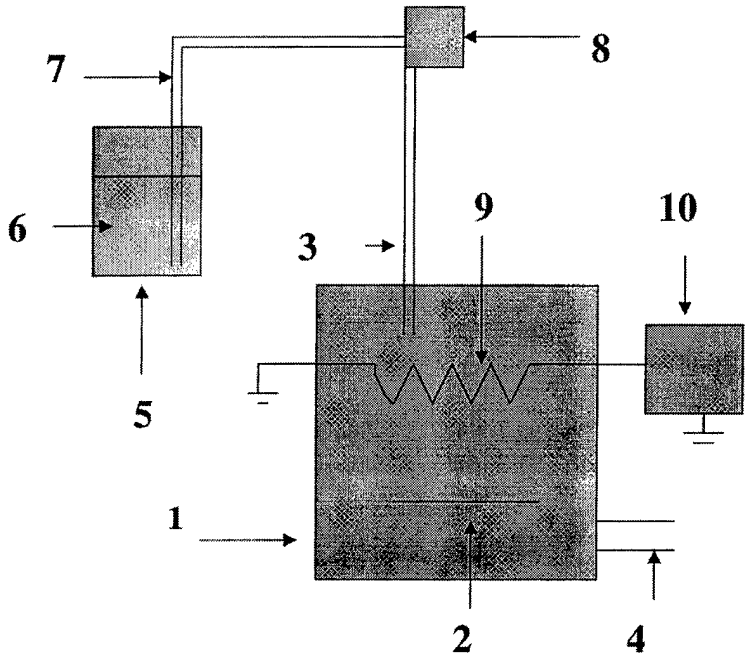

Figure 1. Hot-filament assisted CVD apparatus

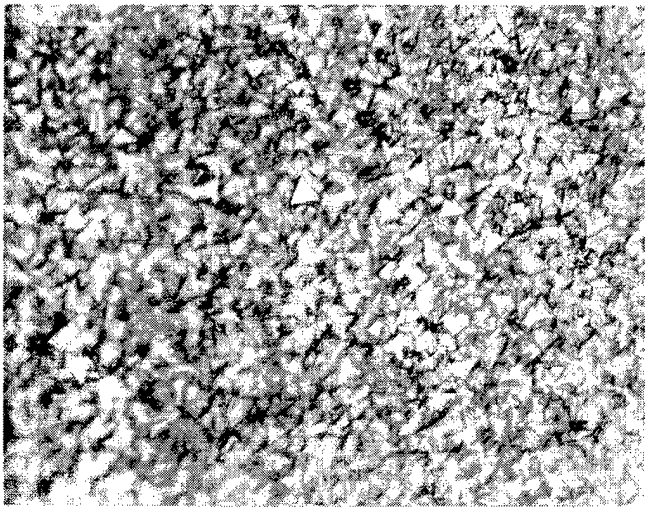

Figure 2. Optical micrograph of a diamond film deposited in the vapor of a solution consisting of 4 grams of ethanol and 100 grams of methanol.

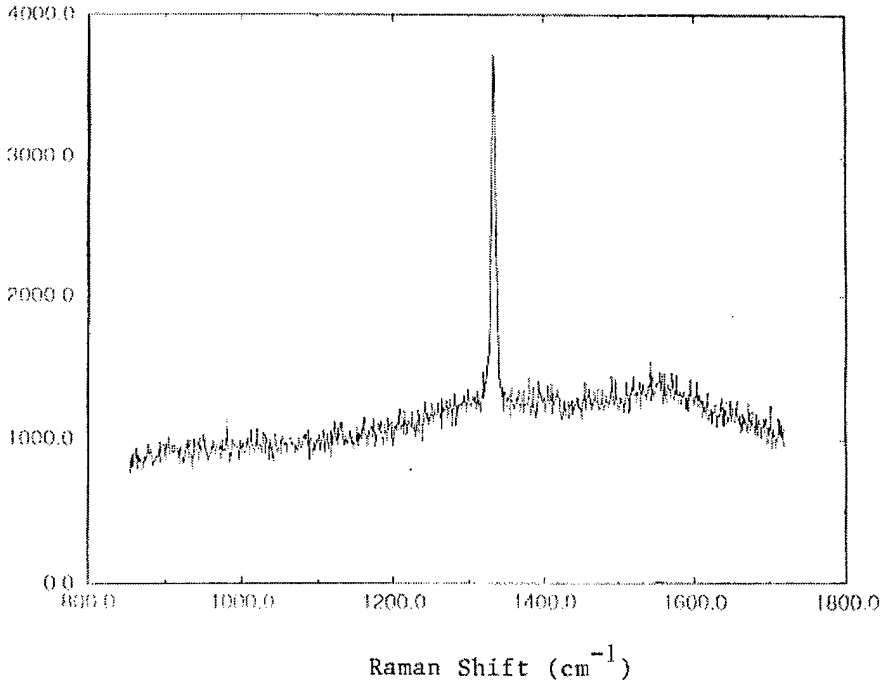

Figure 3. Raman spectrum of the diamond film shown in Figure 2.